CLAIMS
We Claim:

1. A process for the preparation of dialkyl carbonate comprising:

reacting carbon monoxide, at least one alkanol and an oxygen-containing gas in the presence of a ionic halogen free copper catalyst, thereby forming said dialkyl carbonate in a crude dialkyl carbonate product.

2. The process of claim 1, wherein said catalyst is selected from the group consisting of: [1,1'(1-butylbenzimidazol-2yl)pentane]copper(II) di(trifluoromethanesulfonate), [1,1'bis(1-ethylbenzimidazol-2yl)propane]copper(II) di(tosylate), *rac*-[2,2′-bis[2-(1-ethylbenzimidazol-2yl)]biphenyl]copper(II) di(trifluoroacetate), *rac*-[[*S*-2,2′-bis[2-(1-butylimidazol-2yl)]biphenyl]copper(II) di(pentafluorobenzoate, and *rac*-[[*S*-2,2′-bis[2-(1-octylbenzimidazol-2yl)]biphenyl]copper(II) di(pentafluorophenylsulfonate).

3. The process of claim 1, wherein the molar ratio of said carbon monoxide to said oxygen-containing gas is between about 3:1 to about 100:1.

4. The process of claim 1, wherein said reaction step is carried out at a temperature between about 40 °C to about 200 °C and at a pressure between about atmospheric pressure up to about 1400 Mpa.

5. The process of claim 1, wherein said catalyst is present from about 10 g/l to 300 g/l of the total reaction mixture.

6. The process of claim 1, further comprising recovering a dialkyl carbonate enriched stream from said crude dialkyl carbonate product.

7. The process of claim 6, wherein said recovery step is at least one step selected from the group consisting of distillation, filtration, decanting, centrifugation, demixing, absorption on solid absorbents and permeation through selective membranes.

8. The process of claim 1, wherein said alkanol is methanol and said dialkyl carbonate is dimethyl carbonate.

9. The process of claim 8, wherein said alkanol is present in a concentration from about 30 wt% to about 95 wt% of the total reaction mixture.

10. The process of claim 8, further comprising water in a concentration from about 1 wt% to about 10 wt% of the total reaction mixture.11.The process of claim 1, further comprising an inert gas.

11. The process of claim 11, wherein said inert gas is selected from the group consisting of nitrogen, argon and a mixture thereof.

12. The process of claim 1, wherein said catalyst is a homogeneous catalyst.

13. The process of claim 1, wherein said catalyst is a heterogeneous catalyst.

14. The process of claim 1, wherein said catalyst comprises a support.

15. The process of claim 15, wherein said support comprises at least one material selected from the group consisting of alumina, silica, and a polymeric material.

16. The process of claim 1, wherein said process is a continuous process.

17. The process of claim 1, wherein said process is a batch process.

18. A composition useful for the preparation of dialkyl carbonates, the composition comprising:

an ionic halogen free catalyst;

carbon monoxide;

an alkanol; and

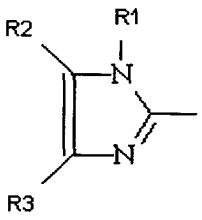
an oxygen-containing gas.

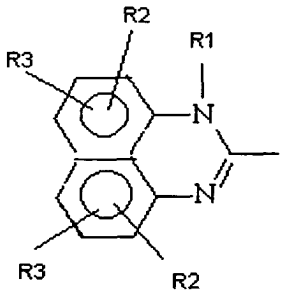
19. The composition of claim 1, wherein the ionic halogen free catalyst has the formula LM X_1 X_2, wherein X_1 and X_2 are independently selected from the group consisting of hydride, triflate, acetate, trifluoroacetate, perfluorotetraphenyl borate, tetrafluoro borate, C_1 through C_{12} straight chain or branched alkyl or alkoxy, C_3 through C_{12} cycloalkyl or cycloalkoxy, and aryl, wherein M is selected from the group consisting of Cu, Ag, and Au; and wherein L comprises a nitrogen-containing bidentate ligand with more than 2 nitrogen atoms.

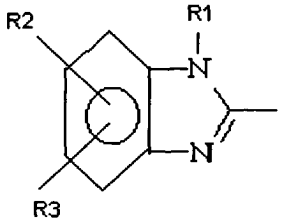
20. The composition of claim 21, wherein L comprises a nitrogen-containing bidentate ligand represented by the formula:

[AZA'] and [AA'],

wherein A and A' are independently selected from the group consisting of







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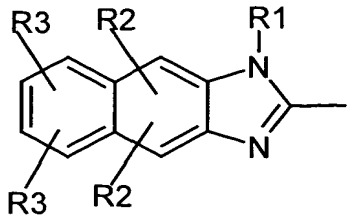

wherein R1 is independently selected from the group consisting of hydrogen, C_1 through C_{12} straight chain or branched alkyl, C_3 through C_{12} cycloalkyl, aryl, and trifluoroethane; R2 and R3 are independently selected from the group consisting of hydrogen, C_1 through C_{12} straight chain or branched alkyl, C_3 through C_{12} cycloalkyl, C_1 through C_{12} alkoxy, F, Cl, SO_3, C_1 through C_{12} perfluoroalkyl, and $N(CH_3)_2$; wherein Z is selected from the group consisting of non-substituted C_1, through C_{12} alkyl, C_3 through C_{12} cycloalkyl; methoxy; amino; halo; C_1, through C_{12} haloalkyl substituted alkyl, cycloalkyl of up to 12 carbon atoms, C_1 -C_{40} aryl; and C_1 -C_{40} alkylaryl; and wherein X_1 and X_2 are independently selected from the group consisting of hydride, triflate, acetate, trifluoroacetate, perfluorotetraphenylborate, tetrafluoroborate, C_1, through C_{12} alkyl, C_1, through C_{12} alkoxy, C_3 through C_{12} cycloalkyl, C_3 through C_{12} cycloalkoxy, and aryl.